



# Effect of periodic lean/rich switch on methane conversion over a Ce–Zr promoted Pd–Rh/Al<sub>2</sub>O<sub>3</sub> catalyst in the exhausts of natural gas vehicles

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## ABSTRACT

The behavior of a commercial Ce–Zr promoted Pd–Rh/Al<sub>2</sub>O<sub>3</sub> catalyst for the abatement of methane from the exhausts of natural gas vehicles (NGVs) is studied in presence of large amounts of water under both stationary conditions and by periodically switching from lean to rich feed. Under stationary conditions with both stoichiometric ( $\lambda = 1.00$ ) and lean ( $\lambda = 1.02$ ) feed catalyst deactivation is observed after prolonged exposure to the reaction mixture. Periodic rich pulses in a constant lean feed gas result in the stabilization of catalytic performances.

A higher methane conversion than those obtained with stoichiometric and lean feed mixtures is observed under rich conditions, during an experiment carried out by performing lean pulses ( $\lambda = 1.02$ ) in a constant rich feed gas ( $\lambda = 0.98$ ). The analysis of reactants conversion and products distribution suggests that different chemistries are involved under lean and rich conditions. Only reactions of complete oxidation of H<sub>2</sub>, CO, CH<sub>4</sub> and NO occur under excess of oxygen, whereas under rich conditions NO reduction, CH<sub>4</sub> steam reforming and water gas shift also occur.

The effect of symmetric oscillation of the exhausts composition around stoichiometry is also addressed by periodically switching from slightly rich to slightly lean composition with different oscillation amplitudes ( $\Delta\lambda = \pm 0.01$ ,  $\pm 0.02$  and  $\pm 0.03$ ). Higher and more stable methane conversion performances are obtained than those observed under constant  $\lambda$  operations. The presence of a more active PdO/Pd<sup>0</sup> state is suggested to explain the enhancement of catalytic performances.

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## 1. Introduction

Natural gas vehicles (NGVs) have been introduced in the market since a long time. However, at present the low number of filling stations and the problems related to the storage of gaseous fuels limit their diffusion. Nevertheless, the use of compressed natural gas (CNG) in automotive applications is of wide interest primarily for the need to diversify energy sources and for the large worldwide resources of natural gas. Besides, NGVs represent a “green” alternative to gasoline and diesel engines because of the very low sulfur content and the reduced NO<sub>x</sub> and particulate emissions when operating under lean conditions. Furthermore CH<sub>4</sub> (which is the main component of NG exhausts) has the highest hydrogen content, which allows achieving a reduction of CO<sub>2</sub> per MJ emissions with respect to other hydrocarbon fuels. However, the abatement of unburned methane, which constitutes about 90% by volume of NG, still remains a demanding challenge in view of the 100 mg/km limit introduced in EU5/EU6 regulations for total hydrocarbon (THC),

since the methane molecule is very stable and requires high temperatures to be oxidized.

Stoichiometric and lean burn combustion systems are commonly used in NGV, working respectively with a stoichiometric mixture of fuel and air and with an excess of oxygen [1]. The lean-burn technology guarantees an efficient fuel use and a reduction of CH<sub>4</sub> emissions in comparison with stoichiometric engines. However it requires complex aftertreatment systems usually composed of a first catalyst for the oxidation of carbon containing compounds followed by a second catalyst for NO<sub>x</sub> reduction. On the contrary, the aftertreatment systems of the exhausts from stoichiometric engines are simpler, relying predominately on three-way catalysts (TWCs) technology adapted from gasoline applications. In both lean and stoichiometric systems noble metals are employed as active components, among which Pd is predominantly used due to its high activity in CH<sub>4</sub> oxidation [2,3]. It is well known in the literature that the oxidation state of palladium plays a major role on CH<sub>4</sub> oxidation activity of Pd catalysts [4]. Accordingly periodically oscillating lean/rich conditions, which are intrinsic in operation of TWCs and can be forced in operation strategies of lean systems [5], may seriously affect the emission abatement performances. Although a large number of papers have been devoted to the study

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**Table 1**  
Standard mixture composition.

CH <sub>4</sub>	CO	H <sub>2</sub>	NO	O <sub>2</sub>	H <sub>2</sub> O	CO	N <sub>2</sub>	λ	GHSV
0.15 vol.%	0.6 vol.%	0.1 vol.%	0.13 vol.%	0–1.14 vol.%	10 vol.%	10.7 vol.%	Balance	0.97–1.03	50,000 h <sup>−1</sup>

of TWCs under periodic operation, there is no agreement between the results: both improvements [6–10] and negative effect [11–13] in hydrocarbon conversion were found when working under oscillating conditions. However most of them refer to the exhausts of gasoline vehicles, largely represented by hydrocarbons of high molecular weight, which are relatively easy to oxidize, whereas only a few studies are devoted to periodic operation in the exhausts of NGVs [10].

In this work the activity of a commercial Ce–Zr promoted Pd–Rh/Al<sub>2</sub>O<sub>3</sub> catalyst was studied under stationary stoichiometric and lean conditions in presence of large amounts of water. The effect of periodic rich pulses in a constant lean gas mixture and periodic lean pulses in a constant rich gas mixture was also investigated. Symmetric oscillations of gas composition around stoichiometry were also performed by periodically switching the feed from slightly rich to slightly lean compositions with different cycle periods and oscillation amplitudes.

## 2. Experimental

### 2.1. Catalyst

A commercial Pd–Rh based catalyst developed by Ecocat in the form of a 400 CPSI/6 mils washcoated ceramic honeycomb containing 7.1 g/l of Pd:Rh (39:1 of loading) has been used in this study. The washcoat material content referred to the geometric area of the catalyst is 50 g/m<sup>2</sup>. The catalyst coating consists of layered washcoat mainly containing stabilized Al<sub>2</sub>O<sub>3</sub>. In addition, Ce–Zr mixed oxide (Zr/Ce = 3.5) were used to improve the oxygen storage capacity (OSC) of the catalyst and transition metal compounds were used as stabilizers and promoters. The catalyst was prepared by mixing the washcoat materials with precursor salts in a water slurry and then coating to a layered structure.

### 2.2. Experimental setup

The experimental rig for reaction tests consists of 5 lines for the individual feeding of a multifuel mixture (composed of 3 vol.% CH<sub>4</sub>, 12 vol.% CO, 2 vol.% H<sub>2</sub> in N<sub>2</sub>), nitrogen monoxide (1.535 vol.% NO in N<sub>2</sub>), air, carbon dioxide and nitrogen, all coming from cylinders. Each feed line is equipped with a programmable Brooks Instruments mass flow controller. Furthermore, a HPLC pump/evaporator system is used to feed H<sub>2</sub>O. H<sub>2</sub>O concentration was continuously monitored by means of a humidity sensor (Vaisala HUMICAPP – HMT334).

The desired lambda values were obtained by stepwise variations of oxygen concentration, according to the following expression derived from stoichiometric mass balances on a natural gas engine [14]:

$$\lambda = \frac{y_{O_2, \text{air}}}{2} \frac{4y_{CH_4} + 3y_{CO} + 3y_{H_2} - 2y_{O_2} - y_{NO} - 4}{(y_{CO} + y_{H_2} - 2)y_{O_2, \text{air}} + (2y_{O_2} + y_{NO} - y_{CO} - y_{H_2} - 4y_{CH_4})} \quad (1)$$

where  $y_i$  is the molar fraction of  $i$  species.

The individual gas streams were mixed, together with steam, immediately upstream the reaction section, where the lambda value was monitored by an ETAS LA4-4.9 Lambda Meter.

A standard feed gas mixture, representative of the typical exhausts composition from stoichiometric CNG [15], was used,

consisting of 0.15 vol.% CH<sub>4</sub>, 0.6 vol.% CO, 0.1 vol.% H<sub>2</sub>, 0.13 vol.% NO, 0.58 vol.% O<sub>2</sub>, 10 vol.% H<sub>2</sub>O, 10.7 vol.% CO<sub>2</sub> and balance N<sub>2</sub> (see Table 1).

6 × 6 channels catalyst samples with a length of 1.3 cm and total volume of 0.832 cm<sup>3</sup> were cut from the central part of the commercial catalyst and tested as detailed below. The total gas flow was 700 cm<sup>3</sup>/min at NTP in all the experiments, corresponding to a gas hourly space velocity (GHSV) of 50,000 h<sup>−1</sup> referred to the honeycomb catalyst volume.

The monolithic sample was placed inside a stainless steel tubular reactor (Fig. 1) externally heated by an oven. The upstream section of the reactor is filled by quartz spheres (2.6 mm of diameter) to allow complete mixing and preheating of gas feed. The sample was wrapped by a quartz wool tape and located in a properly designed holder to avoid by-pass phenomena.

A sliding thermocouple was inserted into one of the central channels of the monolith for the measurement of the axial gas temperature profile during the experiments. A second thermocouple was located immediately before the entrance of the monolith sample. A good reproducibility of the axial temperature profiles measured during steady state at the same experimental conditions was observed. Moreover, the axial profiles show a smooth maximum close to inlet section, likely associated with fast consumption of CO (and H<sub>2</sub>) which were completely converted at all the investigated temperatures. Overall temperature differences along the catalyst bed are limited within 10–15 °C, i.e. much lower than the overall adiabatic temperature raise (92 °C) of full reactants conversion, indicating that temperature effects are kept limited thanks to strong heat dispersion due to the small size of the catalyst sample. In the following, unless differently specified, monolith temperatures refer to the value measured by the sliding thermocouple immediately after the catalyst entrance.

The analysis of inlet and outlet gas composition was periodically accomplished using a Micro GC (3000 A, Agilent Technologies) equipped by TCD detectors, a Molecular Sieve 5 Å column for separation of N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and CO (Ar carrier) and a Plot Q column for separation of CO<sub>2</sub> and H<sub>2</sub>O. Furthermore, a UV spectrometer (ABB Limas-11HV) was installed for the continuous analysis of NO, NO<sub>2</sub> and NH<sub>3</sub>. This was followed by a condenser for the abatement of NH<sub>3</sub> and water and by a series of gas analyzers (ABB A02020) for continuous monitoring of H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub> outlet concentrations during testing under dynamic conditions. In particular, the analysis of H<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub>–CO–CO<sub>2</sub> was performed by using a thermal conductivity analyzer (ABB Caldos-17), a paramagnetic analyzer (ABB Magnos-106) and an IR spectrometer (ABB Uras-14), respectively. A periodic calibration was performed by means of sample gas with composition close to the feed one. The accuracy of the continuous gas analyzers was within 0.25% and 1% of the calibration span gas. All the output of the analyzers have been synchronized by taking into account the characteristic delay of any specific instrument calculated by means of blank experiments with concentration steps.

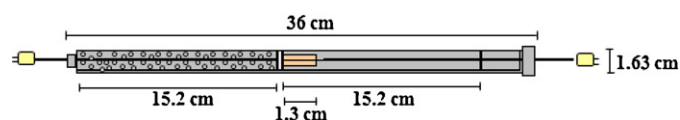


Fig. 1. Stainless steel reactor.

### 2.3. Catalytic activity tests

Before starting an experimental campaign, each monolithic sample underwent a conditioning treatment (*degreening*) in a stoichiometric flow mixture for 5 h @  $T_{\text{oven}} = 600^\circ\text{C}$ .

After degreening, nearly isothermal experiments were carried out under stationary stoichiometric ( $\lambda = 1.00$ ) and lean ( $\lambda = 1.02$ ) conditions. During this type of experiment the reaction mixture was fed to the reactor after preheating the oven at  $200^\circ\text{C}$  in order to avoid water condensation; then the heating of the catalyst was accomplished under the reaction mixture, until reaching an almost stationary temperature ( $T_{\text{oven}} = 450^\circ\text{C}$ ). This temperature was kept constant for at least 30 min, during which the activity was recorded. This procedure was repeated after several hours of time on stream, to check the activity of the catalyst after prolonged exposure to the reaction mixture at different conditions.

The same procedure was adopted over a fresh catalyst sample to perform tests under both periodic pulses and symmetric oscillating  $\lambda$  conditions at an almost stationary oven temperature ( $450^\circ\text{C}$ ). Periodic pulses were accomplished by performing every 5 min 10 s long rich (or lean) pulses ( $\lambda = 0.98$  and  $1.02$ , respectively) on a stationary lean (or rich) feed gas mixture ( $\lambda = 1.02$  and  $0.98$ , respectively), as shown in Fig. 2a and b. Lambda changes were obtained by switching the  $\text{O}_2$  concentration from  $0.20\%$  ( $\lambda = 0.98$ ) to  $0.95\%$  ( $\lambda = 1.02$ ).

As regarding the symmetric oscillating experiments, lambda oscillation amplitudes between  $\pm 0.01$  and  $\pm 0.03$  at constant cycle period (60 s) have been investigated (Fig. 2c).  $\lambda$  oscillations were obtained by periodically switching the set point of the oxygen mass flow controller, to values corresponding to an oxygen concentration oscillating between  $0.38$ – $0.76$  vol.%,  $0.2$ – $0.95$  vol.% and  $0$ – $1.14$  vol.%, respectively. The changes in the oxygen concentration were compensated by simultaneously switching  $\text{N}_2$  feed flow, so that a constant total gas flow of  $700\text{ cm}^3/\text{min}$  was maintained during periodic operations.

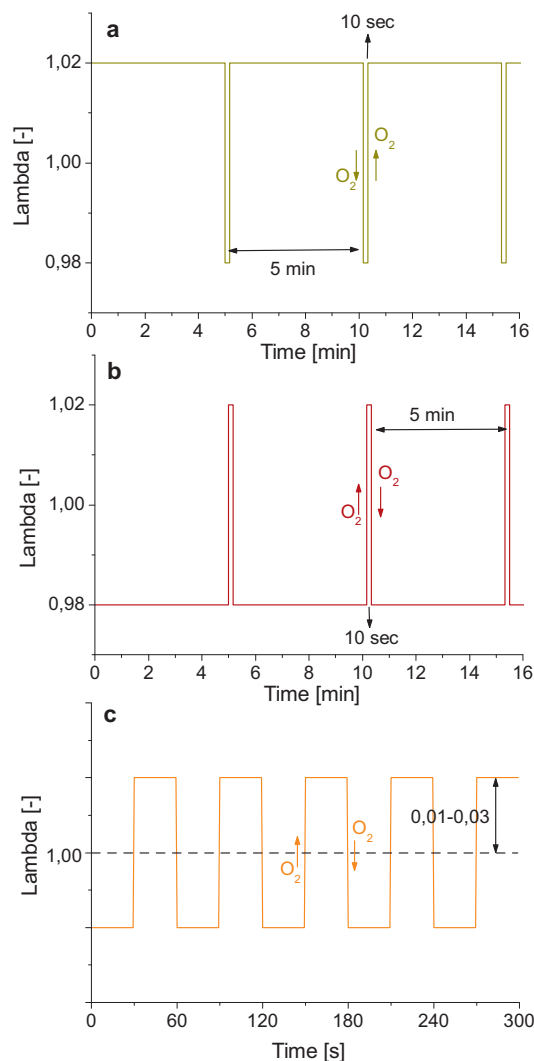
A sequence of experiments at different temperatures (in the range  $200$ – $550^\circ\text{C}$ ) was also performed under stationary rich conditions ( $\lambda = 0.967$ , absence of both  $\text{O}_2$  and  $\text{NO}$ ). The reaction mixture was fed to the reactor after preheating the oven at  $200^\circ\text{C}$ , and then the reaction temperature was kept constant at  $200^\circ\text{C}$  for the time needed to reach a steady state outlet composition (30 min). Then, the catalyst was heated by imposing an increase of  $50^\circ\text{C}$  ( $10^\circ\text{C}/\text{min}$  heating rate) in the oven temperature until a new steady state was reached. This procedure was repeated by imposing  $50^\circ\text{C}$  temperature steps until reaching a maximum oven temperature of  $550^\circ\text{C}$ .

## 3. Results and discussion

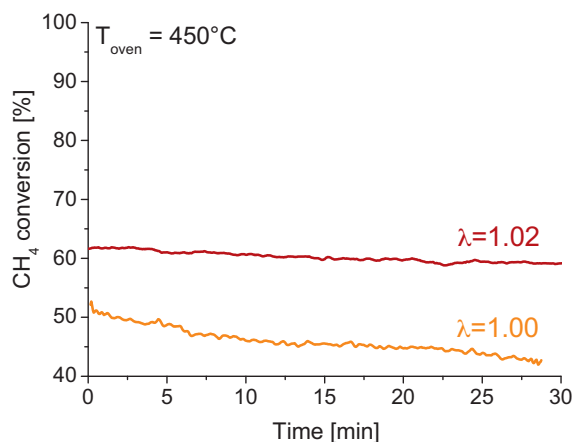
### 3.1. Testing under stationary lean and stoichiometric conditions

The methane combustion activity of the commercial Ce–Zr promoted Pd–Rh/ $\text{Al}_2\text{O}_3$  catalyst provided by Ecocat was measured in a nearly isothermal experiment performed at stationary  $\lambda = 1.00$  and  $T_{\text{oven}} = 450^\circ\text{C}$ ; this corresponds to a measured temperature just after the monolith entrance of about  $470^\circ\text{C}$ , in view of the exothermicity of the reactions.  $\text{CH}_4$  conversion is plotted as a function of time in Fig. 3. A decrease in  $\text{CH}_4$  conversion is observed, passing from  $52$  to  $43\%$  after 30 min. Furthermore, after prolonged exposure to the reaction mixture (11.5 h of operation at different temperatures), the same experiment at  $\lambda = 1.00$  and  $T_{\text{oven}} = 450^\circ\text{C}$  was repeated and  $15\%$  of methane conversion was registered, which proves that the deactivation process went on to a significant extent.

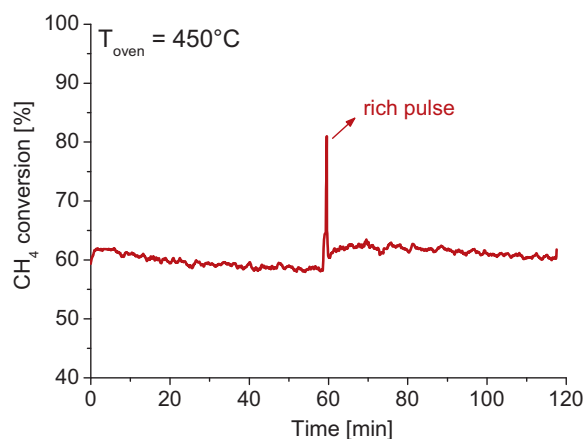
A similar experiment was performed under stationary slightly lean conditions ( $\lambda = 1.02$ ). The results, reported on the same figure (Fig. 3), show again a decrease in  $\text{CH}_4$  conversion, even if in a



**Fig. 2.** Periodic pulses experiments accomplished by performing every 5 min (a) 10 s long rich pulses ( $\lambda = 0.98$ ) on a stationary lean feed gas mixture ( $\lambda = 1.02$ ) and (b) 10 s long lean pulses ( $\lambda = 1.02$ ) on a stationary rich feed gas mixture ( $\lambda = 0.98$ ). (c) Symmetric oscillating experiments: cycle period of 60 s and lambda oscillation amplitudes between  $\pm 0.01$  and  $\pm 0.03$ .



**Fig. 3.** Comparison between  $\text{CH}_4$  conversions under stationary lean ( $\lambda = 1.02$ ) and stoichiometric ( $\lambda = 1.00$ ) feed gas mixture, ( $T_{\text{oven}} = 450^\circ\text{C}$ ).



**Fig. 4.** Effect of a rich pulse ( $\lambda = 0.98$ ) on  $\text{CH}_4$  conversions under stationary lean ( $\lambda = 1.02$ ) feed gas mixture ( $T_{\text{oven}} = 450^\circ\text{C}$ ).

minor extent, passing from 62 to 59% after 30 min. Moreover, after prolonged exposure to the lean reaction mixture (90 h of operation at different temperatures), methane conversion stabilizes around 10%, showing that the deactivation process proceeded as well under lean conditions to a significant extent.

It is worth to note that when working under lean conditions a higher activity for methane oxidation is obtained in comparison with the stoichiometric case (Fig. 3). This effect is likely ascribable to a positive effect of oxygen concentration when working close to stoichiometric conditions [10].

The decay in methane conversion observed at  $\lambda = 1.00$  could be explained by a partial reduction of palladium oxide due to the low oxygen partial pressure, since in the literature the active form of palladium is considered to be either the oxide or a mixture of oxide and metal [16–18], as also confirmed by more recent EXAFS studies [19,20]. However, the reduction of palladium oxide in a stoichiometric atmosphere is unlikely since the catalyst contains oxygen storage materials which can act as oxygen buffer.

Furthermore, catalyst deactivation is also observed under excess of oxygen, as shown by the data collected at  $\lambda = 1.02$ , when a substantial reduction of palladium can be reasonably excluded. Different mechanisms have been proposed in literature to explain the deactivation under stationary lean wet conditions over Pd-based catalysts, all involving a negative effect of  $\text{H}_2\text{O}$ . Cullis et al. [21] attributed the deactivation to the formation of inactive  $\text{Pd}(\text{OH})_2$ .

Along similar lines Ciuparu et al. [22–25] by isotopic studies and FTIR measurements evidenced the formation of strongly bound hydroxyls from methane dissociation during combustion reaction over Pd based catalysts. Thus, assuming that the first H abstraction occurs on a Pd–O pair, the origin of catalyst deactivation could be the blockage of the first H abstraction by stable surface hydroxyls. Finally, a different explanation was provided by Monteiro et al. [26] who associated the deactivation in the presence of water with the surface smoothening of PdO crystallites after reaction in excess of  $\text{O}_2$ , in line with previous literature suggestion [17,27]: the consequent decrease of active surface could account for catalyst deactivation.

In order to check the reversibility of the observed catalyst deactivation, an experiment was designed in view of a recent work by Arosio et al. [28,29] where deactivation due to exposure to  $\text{H}_2\text{O}$  containing atmosphere was completely reversed upon reduction/oxidation cycles of Pd particles. The experiment was performed at an oven temperature of  $450^\circ\text{C}$  by carrying out a 10 s rich pulse after 1 h of time on stream under constant lean conditions:  $\text{CH}_4$  conversion is reported in Fig. 4. An appreciable deactivation is observed during the first hour of time on stream (from 62% to

58% of  $\text{CH}_4$  conversion), whereas after the rich pulses the methane conversion is carried back to its initial value, which proved that the deactivation process is reversible under periodic rich pulses due either to decomposition of  $\text{Pd}(\text{OH})_2$  [28] and/or to roughening of the newly formed PdO surface [26].

### 3.2. Effect of periodic lambda variations during lean-rich operation

An experiment was carried on over the Pd/Rh-based catalyst at an oven temperature of  $450^\circ\text{C}$  by performing 10 s long rich pulses ( $\lambda = 0.98$ ) every 5 min in a stationary lean feed gas mixture ( $\lambda = 1.02$ ). Experimental results in terms of  $\text{CH}_4$  conversion,  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and  $\text{NO}$ – $\text{NO}_2$ – $\text{NH}_3$  outlet molar fractions are shown in Fig. 5a–c.

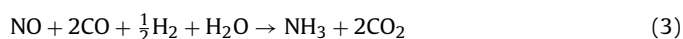
Under lean conditions, after a minimum following each rich pulse (60%),  $\text{CH}_4$  conversion increases till approaching an asymptotic value around 64% (Fig. 5a) while  $\text{H}_2$  (Fig. 5b) and  $\text{CO}$  (not shown) are completely converted. Overall these data confirm the stabilization effect obtained by performing periodic rich pulses.

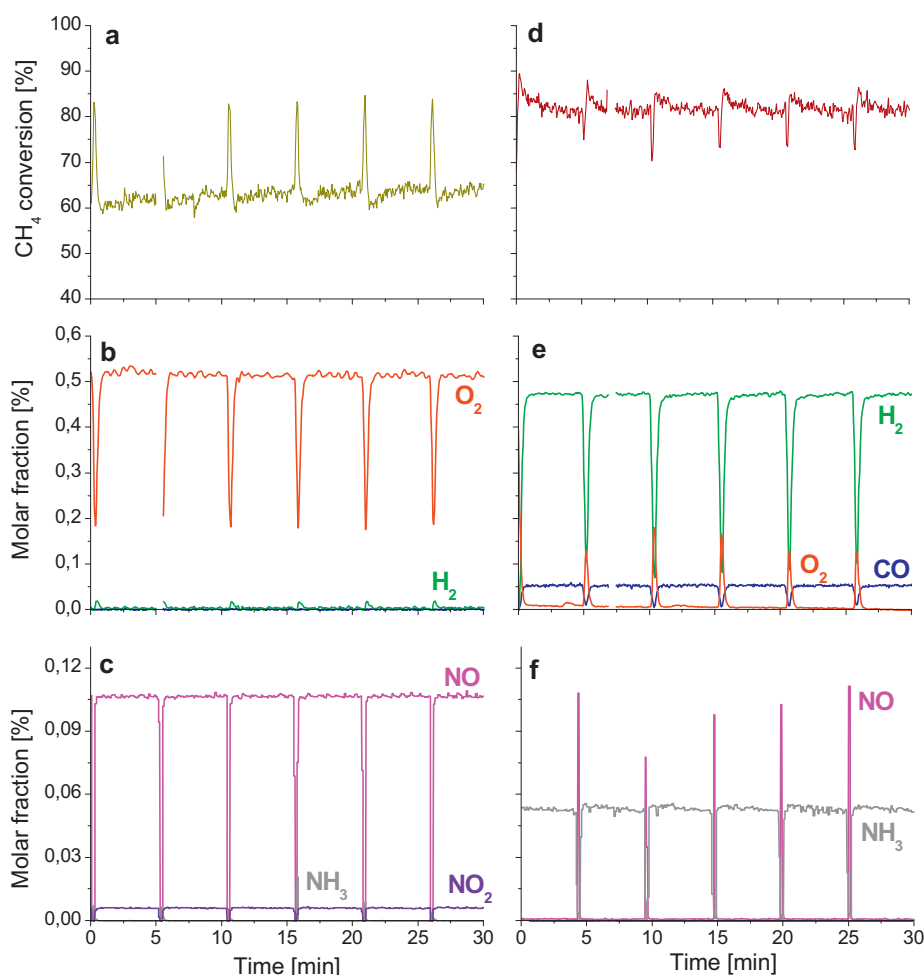
It is also worth of note that about 45% of  $\text{O}_2$  is converted (Fig. 5b), whereas only a small fraction of the  $\text{NO}$  is consumed, accompanied by  $\text{NO}_2$  formation (0.006%), while  $\text{NH}_3$  is not detected (Fig. 5c).

Positive peaks in  $\text{CH}_4$  conversion appear during each rich pulse (see panel a), paralleled by negative peaks of  $\text{O}_2$  and  $\text{NO}$  outlet molar fraction. Simultaneously, the appearance of small amounts of  $\text{H}_2$  and  $\text{NH}_3$  occurs. It is worth noting that, since the characteristic time of the ABB gas analyzers is higher than the pulse duration (10 s) the real changes in composition during rich pulses are wider than those shown in Fig. 5a–c.

In order to obtain a deeper insight into the behavior of the Pd/Rh-based TWC under rich conditions an experiment was carried out at  $T_{\text{oven}} = 450^\circ\text{C}$  by performing periodic 10 s long lean pulses ( $\lambda = 1.02$ ) every 5 min on a stationary rich feed gas mixture ( $\lambda = 0.98$ ). Results in terms of  $\text{CH}_4$  conversion,  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and  $\text{NO}$ – $\text{NO}_2$ – $\text{NH}_3$  outlet molar fractions are shown in Fig. 5d–f. The catalyst undergoes deactivation during the stationary rich period,  $\text{CH}_4$  conversion decreasing from 85 to 81% (Fig. 5d), which is however significantly higher than conversion under lean and stoichiometric conditions, in line with previous results from Subramanian et al. [30]. Besides, it is worth noticing the presence of  $\text{CO}$  (0.054%) in the outlet mixture, together with a net production of  $\text{H}_2$  (0.472% versus 0.1% fed, Fig. 5e) and  $\text{NH}_3$  (0.054%, Fig. 5f) under rich conditions. On the opposite,  $\text{NO}$  and  $\text{O}_2$  are completely consumed. The fact that  $\text{H}_2$  is not consumed, but is rather produced under rich conditions suggests that a different chemistry should be involved under an oxygen deficient atmosphere; steam reforming and water gas shift have to be considered in order to explain hydrogen formation, as it will be discussed in the following. During lean pulses negative peaks of  $\text{CH}_4$  conversion are observed while  $\text{CO}$  and  $\text{H}_2$  are almost completely converted,  $\text{NH}_3$  is absent and positive peaks of  $\text{NO}$  and  $\text{O}_2$  are detected. The different product distributions observed under lean and rich conditions could be explained as follows. For  $\lambda = 1.02$  all the converted  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$  react with oxygen according to the stoichiometries of complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Besides, since a small fraction of the inlet  $\text{NO}$  is converted and  $\text{NO}_2$  is detected at the reactor outlet,  $\text{NO}$  is partially oxidized to  $\text{NO}_2$ .

On the opposite, under rich conditions  $\text{NO}$  is fully consumed, whereas  $\text{CO}$  is still present and a net production of  $\text{H}_2$  and  $\text{NH}_3$  is obtained. In order to explain the formation of  $\text{NH}_3$ , a reaction between  $\text{H}_2$  and  $\text{NO}$  the following stoichiometries could be proposed [31–34]:





**Fig. 5.** Periodic rich pulses ( $\lambda = 0.98$ , 10 s long every 5 min) on a stationary lean feed gas mixture ( $\lambda = 1.02$ ): (a)  $\text{CH}_4$  conversion, (b)  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and (c)  $\text{NO}$ – $\text{NO}_2$ – $\text{NH}_3$  outlet molar fractions. Periodic lean pulses ( $\lambda = 1.02$ , 10 s long every 5 min) on a stationary rich feed gas mixture ( $\lambda = 0.98$ ): (d)  $\text{CH}_4$  conversion, (e)  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and (f)  $\text{NO}$ – $\text{NO}_2$ – $\text{NH}_3$  outlet molar fractions.

Since  $\text{NH}_3$  production is about 40% of  $\text{NO}$  consumption, the remaining fraction of  $\text{NO}$  could likely be reduced to  $\text{N}_2$  or  $\text{N}_2\text{O}$  by  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  [35,36].

Finally, the net production of hydrogen can be explained by the occurrence of steam reforming (SR) and water-gas shift (WGS) reactions:



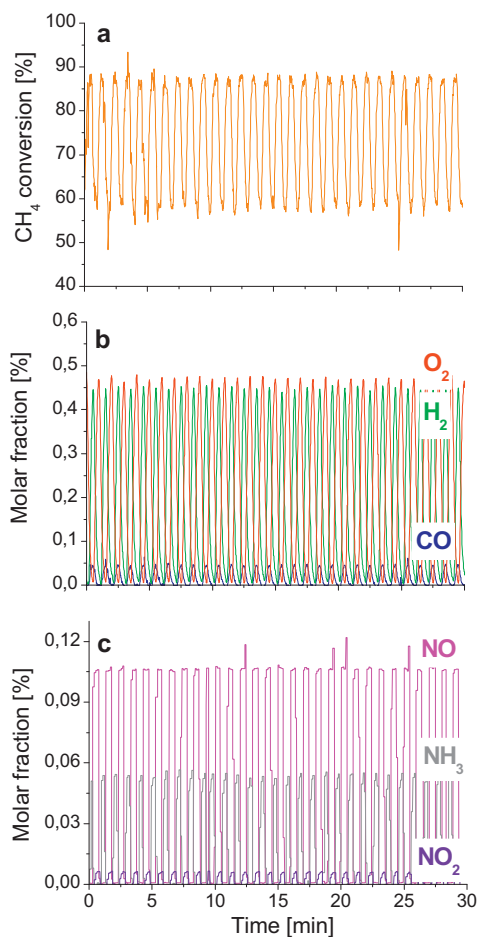
### 3.3. Operations under symmetric periodic lambda oscillations

In order to investigate the effect of periodic operation on methane conversion an experiment was performed at an oven temperature of  $450^\circ\text{C}$  with lambda symmetrically oscillating around the stoichiometric value ( $\lambda = 1 \pm 0.02$ ). A cycle period of 60 s has been used, so to avoid a significant dumping of oscillation measurements due to the characteristic times of the analysis system. The results of this experiment are reported in Fig. 6a–c in terms of  $\text{CH}_4$  conversion,  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and  $\text{NO}$ – $\text{NO}_2$ – $\text{NH}_3$  outlet molar fractions, respectively. Oscillations in the  $\text{CH}_4$  conversion between 58% and 88% and in the outlet molar fractions of  $\text{O}_2$  (0–0.480%),  $\text{H}_2$  (0–0.454%),  $\text{CO}$  (0–0.047%),  $\text{NO}$  (0–0.106%),  $\text{NO}_2$  (0–0.006%) and  $\text{NH}_3$  (0–0.056%) were observed. It is worth noticing that the boundary values obtained during symmetric lambda oscillations for all the observed species are close to the values detected under rich

and lean conditions in the periodic pulse experiments described above (see Fig. 5).

Another experiment was performed at  $T_{\text{oven}} = 450^\circ\text{C}$  under transient conditions by changing every 40 min the amplitude of lambda oscillation ( $\Delta\lambda = \pm 0.01$ ,  $\pm 0.02$  and  $\pm 0.03$ ) and by keeping a constant cycle period ( $t = 60$  s).  $\text{CH}_4$  conversion trends are shown in Fig. 7a. Marked oscillations in  $\text{CH}_4$  conversion are well evident with amplitude increasing with decreasing the extent of  $\lambda$  variations. Calculated cycle average  $\text{CH}_4$  conversion and average  $\text{H}_2$  and  $\text{CO}$  outlet molar fractions are reported in Fig. 7b. A maximum in average  $\text{CH}_4$  conversion (69%) is obtained working with an oscillation amplitude of  $\pm 0.02$ , a slightly lower value (64%) is measured for  $\Delta\lambda = \pm 0.01$ , whereas a more pronounced decrease of  $\text{CH}_4$  conversion (56%) is observed for  $\Delta\lambda = \pm 0.03$ . On the other hand, a linear increase in both  $\text{H}_2$  and  $\text{CO}$  outlet molar fractions is observed while increasing the oscillation amplitude and a similar trend is also observed for  $\text{NH}_3$  formation (not shown). It is worth to note that when operating with symmetric lambda oscillations around stoichiometry the average methane conversions are more stable and higher than those obtained working under stationary stoichiometric ( $\lambda = 1.00$ ) conditions (52%, see Fig. 3).

In order to better clarify the phenomena occurring during periodic operation it can be useful to look into details the single lean/rich cycle in terms of both outlet mixture composition and monolith temperature measured just after the monolith entrance. Panels a, b and c of Fig. 8 report  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and  $\text{CH}_4$  outlet molar



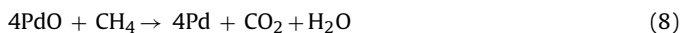
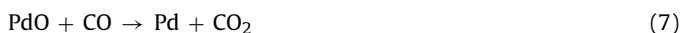
**Fig. 6.** Symmetric  $\lambda$  oscillations ( $\lambda = 1 \pm 0.02$ ,  $t = 60$  s): (a)  $\text{CH}_4$  conversion, (b)  $\text{O}_2$ – $\text{H}_2$ – $\text{CO}$  and (c)  $\text{NO}$ – $\text{NO}_2$ – $\text{NH}_3$  outlet molar fractions.

fractions and monolith temperature for  $\lambda = 1 \pm 0.01$ ,  $\lambda = 1 \pm 0.02$  and  $\lambda = 1 \pm 0.03$ , respectively. In the following analysis one should take into account that the characteristic time of the analysis system causes the smoothing of an original square signal, as it has been demonstrated by blank experiments.

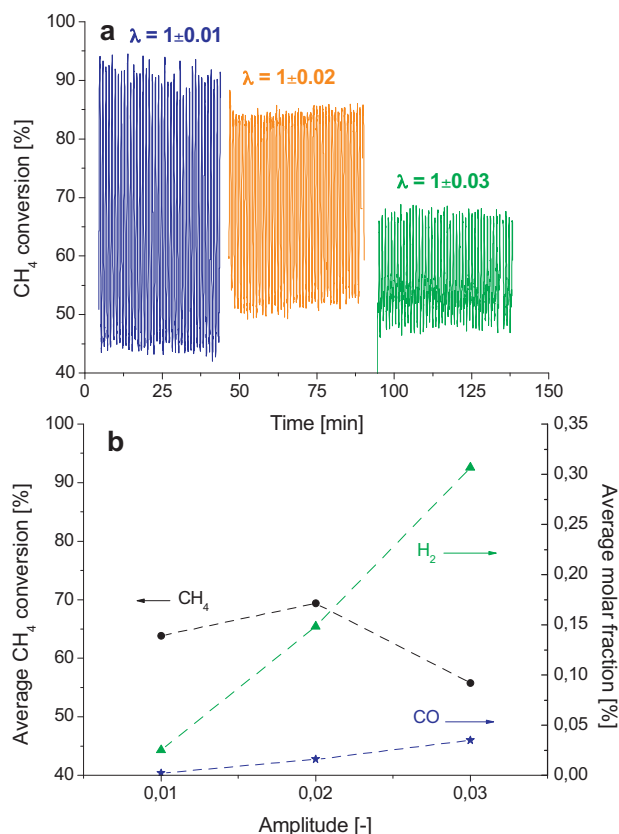
The inspection of the outlet gas composition shows that the oscillation amplitude of outlet  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{CO}$  concentration increases with the amplitude of lambda oscillation (top panels in Fig. 8). Oxygen is always antiphase with hydrogen and carbon monoxide; similarly  $\text{NO}_x$ , which are in phase with  $\text{O}_2$ , are antiphase with ammonia (not reported). It is worth noting that a delay in the oxygen outlet concentration is observed when passing from rich to lean conditions (e.g. at 330 s in Fig. 8b, top panel). Similarly a delay in the  $\text{H}_2$  and  $\text{CO}$  outlet concentrations occurs when passing from lean to rich (e.g. at 360 s in Fig. 8b, top panel).

The observed delays can be explained considering that both palladium and ceria can undergo oxidation/reduction processes when switching forth and back from rich to lean mixtures.

When passing from the lean to the rich atmosphere, reduction of  $\text{PdO}$  by  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  can take place, according to the following reactions:



Since reactions (6)–(8) are fast, it is likely that  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  reduce the  $\text{PdO}$  particles in a shellwise manner according to a



**Fig. 7.** Periodic symmetric  $\lambda$  oscillations at  $T_{\text{oven}} = 450^\circ\text{C}$  with constant cycle period ( $t = 60$  s) and different oscillation amplitude ( $\pm 0.01$ ,  $\pm 0.02$  and  $\pm 0.03$ ): (a)  $\text{CH}_4$  conversions function of time and (b) cycle average  $\text{CH}_4$  conversion and  $\text{H}_2$  and  $\text{CO}$  molar fractions as function of the oscillation amplitude.

shrinking core mechanism [37,38].  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  reduction is also possible, due to the higher redox potential of the couple than that of the  $\text{Pd}^{2+}/\text{Pd}^0$  couple [39]. However, ceria reduction is likely to occur via hydrogen dissociation on Pd and its successive spillover to the support [40,41], thus being a consecutive process with respect to reduction of palladium. Therefore, the observed delays in the  $\text{H}_2$  and  $\text{CO}$  outlet concentrations can be explained by the consumption of these reagents according to reactions (6) and (7) immediately after the switch from lean to rich conditions. On the opposite, a delay in  $\text{CH}_4$  outlet concentration cannot be appreciated because methane is not completely consumed during the lean phase (Fig. 8, central panels).

Similarly, when passing from the rich to the lean phase, metallic Pd is likely oxidized according to the following stoichiometry:

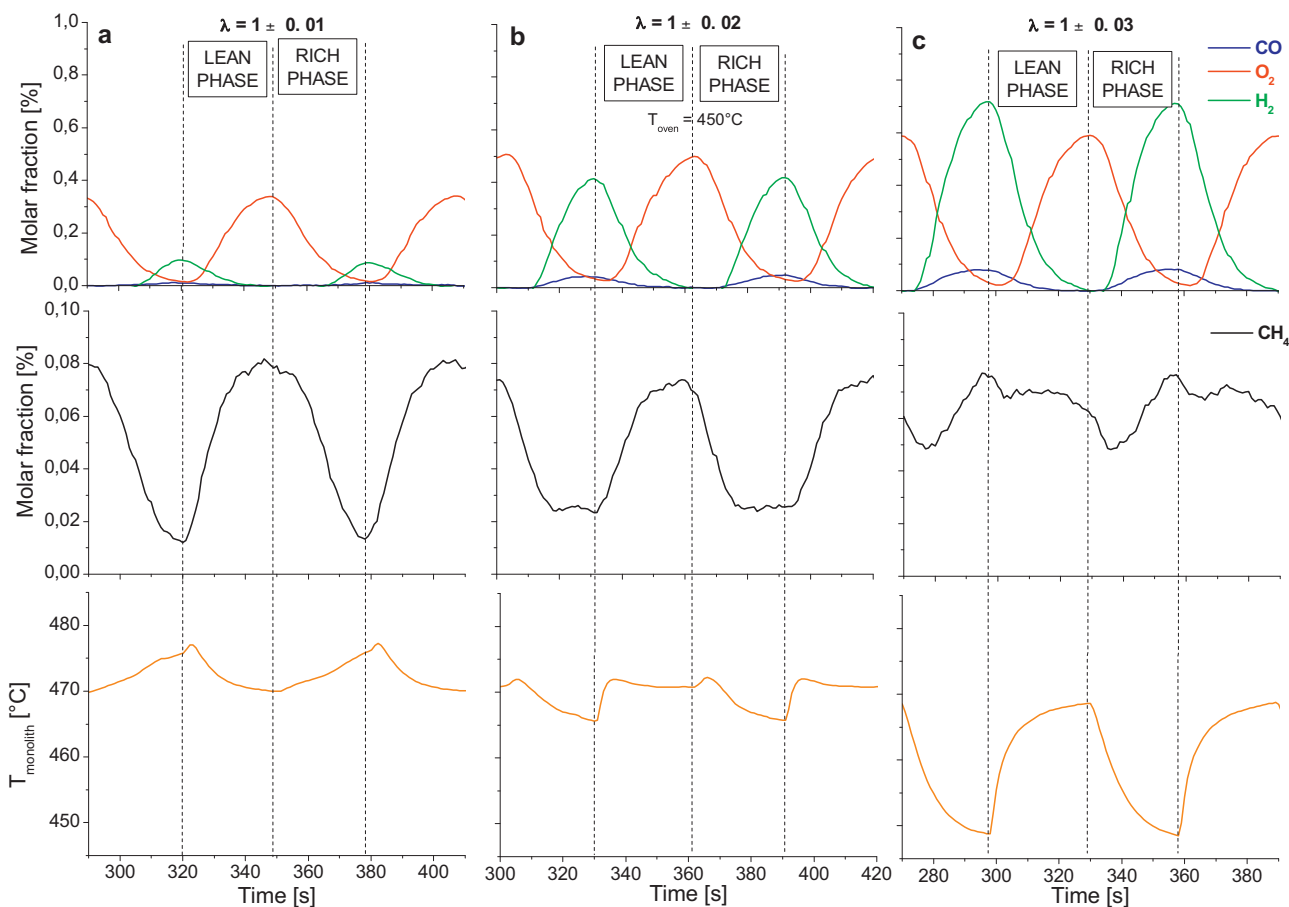


where  $\text{O}_2$  could come directly from the gas phase [38,42] or from ceria lattice [43]. The occurrence of reaction (9), in concomitance with  $\text{Ce}^{3+}$  reoxidation [44], could therefore explain the observed delay in the  $\text{O}_2$  outlet concentration when switching from rich to lean conditions.

Notice that this description could be even further complicated by the presence of a front of palladium (and cerium) oxidation/reduction along the axial coordinate of the monolithic sample during the lean/rich cycles [45].

Surprisingly, in contrast with  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{CO}$ , the oscillation amplitude of outlet  $\text{CH}_4$  concentration decreases on increasing the amplitude of lambda oscillation (Fig. 8, central panels).

For  $\lambda = 1 \pm 0.01$  when switching from rich to lean conditions, the  $\text{CH}_4$  outlet molar fraction increases until reaching a



**Fig. 8.** Outlet molar fractions of CO–O<sub>2</sub>–H<sub>2</sub> and CH<sub>4</sub> and monolith temperature during a single lean/rich cycle: (a)  $\lambda = 1 \pm 0.01$ , (b)  $\lambda = 1 \pm 0.02$  and (c)  $\lambda = 1 \pm 0.03$  ( $t = 60$  s,  $T_{\text{oven}} = 450^\circ\text{C}$ ).

maximum value (0.081%), corresponding to a conversion minimum of 46%. Then, when passing from the lean to the rich phase, a nearly specular decrease in the methane concentration is observed until reaching a minimum value (0.013%), which corresponds to a conversion maximum of 91%.

Similar trends of methane concentrations are observed for  $\lambda = 1 \pm 0.02$ , the boundary values for the lean and the rich phases being 0.073% and 0.023% (corresponding to 51% and 85% of CH<sub>4</sub> conversion), respectively.

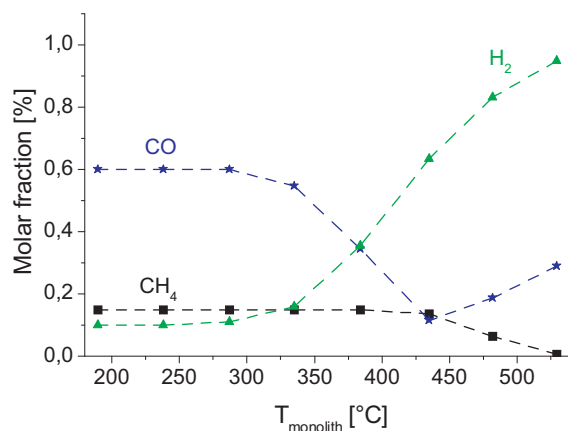
The dynamic of outlet CH<sub>4</sub> concentration in the case of  $\lambda = 1 \pm 0.03$  is more complex. A slight decrease is observed when switching from rich to lean conditions until reaching a value of 0.069% (corresponding to 54% CH<sub>4</sub> conversion). On the other hand when passing from the lean to the rich phase the CH<sub>4</sub> outlet concentration first decreases down to a minimum of 0.047% (corresponding to 69% CH<sub>4</sub> conversion) while CO and H<sub>2</sub> concentration keeps at zero. Then CH<sub>4</sub> concentration starts to increase up to a maximum of 0.077% (corresponding to 48% CH<sub>4</sub> conversion), and H<sub>2</sub> and CO are detected. Therefore the maximum and the minimum CH<sub>4</sub> conversions are obtained at the beginning and at the end of the rich phase, respectively, whereas an intermediate value is reached during the lean phase. Since in this case oxygen is not present in the rich phase, the initial decrease in the CH<sub>4</sub> outlet concentration is likely due to the occurrence of PdO reduction by CH<sub>4</sub> according to reaction (8) along with reactions (6) and (7), which are responsible for complete CO and H<sub>2</sub> consumption.

It is worth noting that the values of CH<sub>4</sub> conversion reached during the lean phase increase with  $\lambda$  (46%, 51% and 54% at  $\lambda = 1.01$ , 1.02 and 1.03, respectively). In all the cases complete conversion of CO

and H<sub>2</sub> is achieved (top panels), and a similar monolith temperature (around 470°C) was measured at the end of the lean phase (bottom panels). This is in line with the effect of O<sub>2</sub> on CH<sub>4</sub> conversion observed in the experiments at constant  $\lambda$  (Fig. 3), confirming that under lean conditions, but in proximity of the stoichiometric composition, CH<sub>4</sub> combustion kinetics has a slightly positive reaction order in O<sub>2</sub> concentration [10].

Also CH<sub>4</sub> conversion levels reached during the rich phase markedly increase with  $\lambda$  (48%, 85% and 91% at  $\lambda = 0.97$ , 0.98 and 0.99, respectively). However, when oscillating around stoichiometry with limited  $\lambda$  variations ( $\pm 0.01$  and  $\pm 0.02$ ), CH<sub>4</sub> conversion obtained during the rich phase is markedly higher than during the lean one. A simple explanation for this behavior could rely on palladium reduction during the rich phase, complete O<sub>2</sub> (and NO) consumption by oxidation of H<sub>2</sub> and CO followed by steam reforming of CH<sub>4</sub> over Pd metal, this latter reaction being faster than CH<sub>4</sub> combustion under oxidising conditions. But data obtained with larger  $\lambda$  oscillations ( $\pm 0.03$ ), when O<sub>2</sub> is absent in the rich phase, show an opposite trend with higher CH<sub>4</sub> conversion in the lean than in the rich phase. Such evidence seems to rule out the hypothesis of higher steam reforming activity under reducing conditions and suggests a major role of O<sub>2</sub> in CH<sub>4</sub> conversion even during the rich phase.

However data interpretation could be biased by thermal effects. In fact inspection of bottom panels in Fig. 8 evidences that temperature measured inside the monolith at the end of the rich phase significantly increases with  $\lambda$  ( $T = 448^\circ\text{C}$ ,  $466^\circ\text{C}$  and  $476^\circ\text{C}$  at  $\lambda = 0.97$ , 0.98 and 0.99, respectively). Such a trend is consistent with the overall exothermicity of the reaction process, which



**Fig. 9.** CH<sub>4</sub>, CO and H<sub>2</sub> outlet molar fractions in function of the monolith temperature during a temperature step experiment in stationary conditions without O<sub>2</sub> and NO ( $\lambda = 0.967$ ).

obviously increases with the O<sub>2</sub> content and could explain the slightly different conversions observed at  $\lambda = 0.98$  and  $0.99$ . Noteworthy at  $\lambda = 0.97$ , i.e. in the absence of O<sub>2</sub>, the temperature is markedly lower than in the corresponding lean phase (Fig. 8c, bottom panel), thus being partly responsible of the observed decrease of CH<sub>4</sub> conversion when switching from lean to rich conditions.

In order to obtain further evidences on the relevance of SR and WGS reactions over the Pd/Rh-based catalyst, a sequence of tests was performed at different temperatures under stationary rich conditions ( $\lambda = 0.967$ ) in absence of both O<sub>2</sub> and NO. Steady state values of CH<sub>4</sub>, H<sub>2</sub> and CO outlet molar fractions are reported in Fig. 9 versus the monolith temperature. A decrease in CO molar fraction was detected starting from 335 °C, accompanied by an equimolar increase in H<sub>2</sub> outlet concentration. A minimum for CO concentration (0.116%) is reached at 435 °C, approaching thermodynamic equilibrium of WGS. It is worth noticing that at 435 °C also methane concentration starts to decrease due to the onset of steam reforming. At higher temperatures CO and H<sub>2</sub> outlet molar fractions increase while CH<sub>4</sub> is rapidly consumed indicating that the steam reforming effectively occurs, being likely promoted by Ce–Zr oxide [39] and Rh [46], which are included in catalyst formulation. Interpolation of data of CH<sub>4</sub> outlet concentration provides an estimate of about 0.014% at 448 °C, corresponding to 24% of CH<sub>4</sub> conversion, which is quite lower than 48% reached during the rich phase in symmetric periodic oscillation experiments with  $\lambda = 1 \pm 0.03$ . This suggests a significant role of NO in CH<sub>4</sub> conversion at  $\lambda = 0.97$ , likely involving Rh [46,47]. Similarly an estimate of 0.083% in pure steam reforming conditions at 470 °C is obtained, corresponding to 45% of CH<sub>4</sub> conversion, which is much lower than 85–90% achieved under rich conditions during symmetric periodic oscillation experiments with  $\lambda = 1 \pm 0.01$  and  $\lambda = 1 \pm 0.02$ , confirming that O<sub>2</sub> plays a major role in CH<sub>4</sub> conversion under slightly rich operations.

A promoting role of O<sub>2</sub> on CH<sub>4</sub> conversion could be ascribed to the occurrence of direct combustion reaction, but this is unlikely due to competition with much more reactive CO and H<sub>2</sub>, which at  $\lambda = 0.98$  are present in a significant excess with respect to complete O<sub>2</sub> (and NO) consumption.

Alternatively, the higher conversion values observed in the presence of O<sub>2</sub> could be explained by the formation of a more active mixed PdO/Pd<sup>0</sup> state, possibly promoted by the presence of Ce–Zr–O, at least in the first section of the monolith bed where O<sub>2</sub> has not been yet totally consumed.

Although the discussion about which state of palladium, metallic [16,48–53] or oxide [17,54–61], is the most active toward CH<sub>4</sub> combustion is still open, some evidences that the copresence of the two phases has a positive effect on the catalyst performance

have been reported by several authors [4,18,62–64]. The presence of a more active mixed PdO/Pd<sup>0</sup> state rather than a fully oxidized one could be also responsible for the CH<sub>4</sub> conversion enhancement observed when switching from the lean to the rich phase at small  $\Delta\lambda$  amplitude and of stabilization of performances by periodic reducing pulses during stationary lean operation.

#### 4. Conclusions

The performances of a commercial Ce–Zr promoted Pd–Rh/Al<sub>2</sub>O<sub>3</sub> catalyst have been studied under both stationary and periodically switching lean/rich conditions.

Results show that operations under stationary lambda conditions lead to progressive decrease of CH<sub>4</sub> conversion. Activity can be recovered by performing rich pulses in a stationary lean feed gas mixture.

Higher and more stable average methane conversions than those obtained under constant  $\lambda$  (lean and stoichiometric) operations are reached when performing symmetric  $\lambda$  oscillations around stoichiometry. It is suggested that the higher conversion performances observed during oscillating conditions could be ascribable to the presence of a more active mixed PdO/Pd<sup>0</sup> state, but further spectroscopic investigations are needed to provide evidence about this picture.

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